

AMORPHOUS COPOLYESTERS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of Application Serial No. 10/743,112 filed December 22, 2003, which is a continuation-in-part of Application Serial No. 10/195,267 filed July 15, 2002, which claims the benefit of United States Provisional Application Serial No. 60/306,221 filed July 18, 2001.

TECHNICAL FIELD OF THE INVENTION

[0002] This invention relates to amorphous copolymers derived from 1,4-cyclohexanedimethanol and neopentyl glycol. More particularly, this invention relates to such copolymers that have a combination of unique properties and to shaped articles fabricated therefrom such as profile extrusions and medical equipment.

BACKGROUND OF THE INVENTION

[0003] Amorphous copolymers comprising terephthalic acid (T) residues and diol residues comprising varying ratios of 1,4-cyclohexanedimethanol (CHDM) residues and ethylene glycol (EG) residues are well known in the plastics marketplace. As used herein, the abbreviation PETG refers to copolymers comprising terephthalic acid residues as the diacid residue component and a diol residue component comprising up to 50 mole percent CHDM residues with the remainder EG residues. PCTG refers to copolymers comprising T residues and a diol residue component comprising greater than 50 mole percent CHDM residues with the remainder being EG residues. Copolymers comprising T residues and diol residues comprising about 20 to 70 mole percent CHDM residues and about 80 to 30 mole percent EG residues are amorphous. The term "amorphous" as defined herein means a polyester that does not exhibit a substantial crystalline melting point when scanned by differential scanning calorimetry (DSC) at a rate of 20°C/minute.

[0004] Amorphous copolymers in general possess a combination of desirable properties for many applications. These properties include excellent clarity and color, toughness, ease of processing, and chemical resistance. Accordingly, amorphous copolymers are known to be useful for the manufacture of extruded sheet, packaging materials, and parts for medical devices, etc. Application in transparent medical parts requires resistance to craze formation and mechanical failure when exposed to lipid and/or isopropyl alcohol (IPA) solutions. Whereas amorphous copolymers are known in the art to have good resistance to these chemicals and are widely applied in these applications, craze formation occurs at high strains and is thus an area of needed improvement. Consequently, there is an unmet need for amorphous copolymers that under high strains have improved resistance to lipid and IPA solutions.

[0005] There is also an important need for amorphous copolymers that have improved resistance to hydrolytic degradation. U.S. Patent 5,656,715 discloses that copolymers containing a diol residue component comprising 60 to 100 mole percent residues of 1,4-cyclohexanedimethanol exhibit improved resistance to hydrolytic degradation.

[0006] Neopentyl glycol (NPG - 2,2-dimethylpropane-1,3-diol) has been used in combination with EG and terephthalic acid to form amorphous copolymers. However, the combination of NPG and CHDM as the diol component of copolymers has received minimal attention. Several early references disclose copolymers comprising both CHDM and NPG residues and terephthalic acid residues. Example 46 of U.S. Patent 2,901,466 describes a copolymer of unknown composition that was reported to have a crystalline melting point of 289-297°C. U.S. Patent 3,592,875 discloses copolymer compositions that contain both NPG and CHDM residues with an added polyol present for branching. U.S. Patent 3,592,876 discloses polyester compositions that contain EG, CHDM and NPG residues with the NPG residue level limited to up to 10 mole percent. U.S. Patent 4,471,108 discloses low molecular weight polyesters some of which contain CHDM and NPG residues, but also contain

a multifunctional branching agent. U.S. Patent 4,520,188 describes low molecular weight copolymers comprising mixtures of aliphatic and aromatic acid residues with both NPG and CHDM residues present. Japanese Patent Publication JP 3225982 B2 discloses amorphous copolymers which are said to be useful in the formulation of coating compositions for steel sheet. The disclosed copolymers comprise a diacid component comprising mixtures of aliphatic and aromatic acid residues and a diol component comprising NPG and CHDM residues.

[0007] U.S. Patent 4,551,403 discloses low molecular weight polyesters that are used as binders or as the matrix resin for photosensitive materials for electrophotography. Example 1 of this patent discloses the preparation of a polymer from dimethyl terephthalate, neopentyl glycol and 1,4-cyclohexanedimethanol. The polymer is said to have a reduced viscosity of 0.35 as measured at 30°C in tetrachloroethane at a polymer concentration of 0.5%. The reduced viscosity of 0.35 corresponds to an inherent viscosity as defined herein of 0.29 dL/g using equations provided by F. W. Billmeyer, *Textbook of Polymer Science*, John Wiley & Sons, (1971) page 84. The low molecular weight polyesters disclosed by US 4,551,403 are not useful for producing shaped articles by injection molding or extrusion procedures.

[0008] EP-A1- 411,136 discloses copolymers comprising diacid residues comprising mainly of terephthalic acid residues and glycol residues comprising 15 to 85 mole percent C-2 to C-16 aliphatic diol residues and 85 to 15 mole percent 1,4-cyclohexanedimethanol residues wherein 80 mole percent of the cyclohexanedimethanol residues are in the trans form. It is believed that the properties of the copolymers specifically exemplified in EP-A1- 411,136 are inferior to the copolymers described herein. More specifically, the copolymers described herein possess improved melt strength and resistance to hydrolysis as compared to the copolymers of the examples of EP-A1- 411,136.

SUMMARY OF THE INVENTION

[0009] We have discovered that amorphous polyesters derived from terephthalic acid, CHDM and NPG are valuable compositions useful for the manufacture of medical devices that exhibit improved resistance to degradation upon exposure to lipids. The amorphous copolymers provided by the present invention have an inherent viscosity (IV) of at least about 0.5 dL/g measured at a temperature of 25°C at 0.5 g/dL concentration in a solvent mixture of symmetric tetrachloroethane and phenol having a weight ratio of symmetric tetrachloroethane to phenol of 2:3 and comprise:

- (1) a diacid component comprising about 90 to 100 mole percent terephthalic acid residues and 0 to about 10 mole percent isophthalic acid residues; and
- (2) a diol component comprising about 10 to about 70 mole percent 1,4-cyclohexanedimethanol residues and about 90 to about 30 mole percent neopentyl glycol residues;

wherein the amorphous copolymers comprises 100 mole percent diacid component and 100 mole percent diol component.

[0010] Another embodiment of the present invention concerns a shaped article such as an extruded profile or an extruded or injection molded medical device having improved resistance to degradation from exposure to lipids wherein the medical device is fabricated or prepared from an amorphous copolymer having an inherent viscosity (IV) of at least about 0.5 dL/g measured at a temperature of 25°C at 0.5 g/dL concentration in a solvent mixture of symmetric tetrachloroethane and phenol having a weight ratio of symmetric tetrachloroethane to phenol of 2:3 and comprising:

- (1) a diacid component comprising about 90 to 100 mole percent terephthalic acid residues and 0 to about 10 mole percent isophthalic acid residues; and
- (2) a diol component comprising about 10 to about 70 mole percent 1,4-cyclohexanedimethanol residues and about 90 to about 30 mole percent neopentyl glycol residues;

wherein the amorphous copolymers comprises 100 mole percent diacid component and 100 mole percent diol component.

[0011] In still another embodiment of the present invention, a method of melt processing an amorphous copolyester having a moisture content prior to melt processing of 0.02 weight % or more comprises the steps of:

- (a) prior to melt processing, performing a minimal drying or no drying of the copolyester such that the copolyester has a moisture content of 0.02 weight % or more prior to melt processing, and
- (b) melt processing the copolyester, wherein the copolyester has an inherent viscosity (IV) of at least about 0.5 dL/g measured at a temperature of 25°C at 0.5 g/dL concentration in a solvent mixture of symmetric tetrachloroethane and phenol having a weight ratio of symmetric tetrachloroethane to phenol of 2:3 and comprises:
 - (1) a diacid component consisting essentially of about 90 to 100 mole percent terephthalic acid residues and 0 to about 10 mole percent isophthalic acid residues; and
 - (2) a diol component consisting essentially of about 10 to about 70 mole percent 1,4-cyclohexanedimethanol residues and about 90 to about 30 mole percent neopentyl glycol residues,

wherein the copolyester is based on 100 mole percent diacid component and 100 mole percent diol component.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 shows the melt viscosity shear rate curve at 260°C for PETG, PROVISTA™, and the amorphous copolyester of the present invention described in Example 10. Figure 2 shows the melt viscosity shear rate curve at 260°C for PETG, PROVISTA™, and the amorphous copolyester of the present invention described in Example 8.

DETAILED DESCRIPTION OF THE INVENTION

[0013] Copolyesters comprising about 90 to 100 mole percent terephthalic acid (T) residues, 0 to about 10 mole percent isophthalic acid residues, 1,4-cyclohexane-dimethanol (CHDM) residues, and neopentyl glycol (NPG) residues are amorphous in the approximate composition ranges of about 10 to about 70 mole% CHDM and about 90 to about 30 mole percent NPG. These unique amorphous copolyesters show surprisingly improved resistance to crazing when exposed to lipids or IPA. In addition, the combination of CHDM and NPG as comonomer diols in the copolyesters of the present invention, results in copolyester backbones that exhibit enhanced stability to hydrolysis for the amorphous composition range. The present copolyesters having sufficient molecular weight to be molding or extrusion grade plastics and based solely on CHDM and NPG as diols, are not known. In addition, it is unexpected that the addition of NPG to a copolyester would improve resistance to lipids and IPA.

[0014] The amorphous copolyesters of the present invention may be prepared by conventional polymerization processes known in the art, such as the procedures disclosed in U.S. Patents 4,093,603 and 5,681,918. Examples of polycondensation processes useful in the present invention include melt phase processes conducted with the introduction of an inert gas stream, such as nitrogen, to shift the equilibrium and advance to high molecular weight or the more conventional vacuum melt phase polycondensations, at temperatures in the range of from about 240 to 300°C or higher which are practiced commercially. The terephthalic and isophthalic acid residues of the copolyesters may be derived from either the dicarboxylic acids or ester-producing equivalents thereof such as esters, e.g., dimethyl terephthalate and dimethyl isophthalate, or acid halides, e.g. acid chlorides. Although not required, conventional additives may be added to the copolyesters of the invention in typical amounts. Examples of such additives include pigments, colorants, stabilizers, antioxidants, extrusion aids, slip agents, carbon black, flame retardants and mixtures thereof.

[0015] The polymerization reaction may be carried out in the presence of one or more conventional polymerization catalysts. Typical catalysts or catalyst systems for polyester condensation are well-known in the art. Suitable catalysts are disclosed, for example, in U.S. Patent Nos. 4,025,492, 4,136,089, 4,176,224, 4,238,593, and 4,208,527, the disclosures of which are herein incorporated by reference. Further, R.E. Wilfong, *Journal of Polymer Science*, 54, 385 (1961) describes typical catalysts, which are useful in polyester condensation reactions. Preferred catalyst systems include Ti, Ti/P, Mn/Ti/Co/P, Mn/Ti/P, Zn/Ti/Co/P, Zn/Al. When cobalt is not used in the polycondensation, copolymerizable toners may be incorporated into the copolyesters to control the color of these amorphous copolyesters so that they are suitable for the intended applications where color may be an important property. In addition to the catalysts and toners, other additives, such as antioxidants, dyes, etc. may be used in the copolyesterifications.

[0016] The copolyesters of the invention have an inherent viscosity (IV) of at least about 0.5 dL/g, preferably about 0.5 to 1.1 dL/g, measured at a temperature of 25°C at 0.5 g/dL concentration in a solvent mixture of symmetric tetrachloroethane and phenol having a weight ratio of symmetric tetrachloroethane to phenol of 2:3. In one embodiment of the invention, the diacid component of the amorphous copolyester consists essentially of about 90 to 100 mole percent terephthalic acid residues and 0 to about 10 mole percent isophthalic acid residues; and the diol component consists essentially of about 10 to about 70 mole percent 1,4-cyclohexanedimethanol residues and about 90 to about 30 mole percent neopentyl glycol residues. Preferably, the diacid component consists essentially of at least 95 mole percent and more preferably 100 mole percent terephthalic acid. The diol component preferably consists essentially of residues of about 30 to about 70 mole percent or, more preferably, about 35 to about 60 mole percent, CHDM residues and about 70 to about 30 mole percent or, more preferably, about 40 to about 65 mole percent, NPG residues. The most preferred copolyesters have an IV of about 0.60 to about 1.1 dL/g and comprise:

- (1) a diacid component consisting essentially of terephthalic acid residues; and
- (2) a diol component consisting essentially of about 35 to about 60 mole percent 1,4-cyclohexanedimethanol residues and about 40 to about 65 mole percent neopentyl glycol residues;

wherein the amorphous copolymers comprises 100 mole percent diacid component and 100 mole percent diol component.

[0017] The copolymers of the invention can be molded and extruded using conventional melt processing techniques to produce the shaped article of our invention. The copolymers are particularly useful in the manufacture of small and intricately shaped articles such as tubing used for handling and transporting medical fluids, etc. The lipid resistance of the copolymers of our invention under external strain renders the copolymers particularly useful in the manufacture of shaped articles including medical devices such as tubes, pump housings, connectors, etc. where lipid resistance is important. Such medical devices may be transparent. The shaped articles manufactured from the copolymers of this invention possess improved resistance to degradation by medical lipid solutions such as Liposyn II 20% intravenous fat emulsion. The improved resistance to degradation is manifested by retention of elongation to break values (retention of toughness) and significant reduction of visual crazing in molded test bars as shown in the examples below.

[0018] The shaped articles may be produced according to conventional thermoplastic processing procedures such as injection molding, calendaring, extrusion, blow molding, extrusion blow molding, and rotational molding. The amorphous copolymers of the present invention derived from CHDM and NPG exhibit improved hydrolytic stability at various melt temperatures. In the conversion of the copolymers into shaped articles, the moisture content of the copolymer typically is reduced to less than about 0.02% prior to melt processing.

[0019] Preferably, prior to melt processing, the minimal drying is performed by conventional methods for less than 2 hours at 60 to 100°C. For the minimal drying, a

desiccant bed with forced dehumidified air at 60°C to 100°C is preferred. Even more preferably, there is no drying of the copolyester prior to melt processing.

[0020] The melt viscosity versus shear rate relationship in polymers is a very important property of polymeric materials. One useful melt viscosity/shear rate relationship is shear thinning. Shear thinning occurs when the melt flow is non-Newtonian and shows a reversible decrease in viscosity with increasing shear rate. Shear thinning characteristics are very important for allowing the processing of injection molded and extruded parts and sheets, such as profiles. Profile extrusion is an extrusion process where special dies are used to produce articles of asymmetrical shapes. House siding, plastic tubes, channels, baseboard moldings, etc. are examples of profile extruded parts and are referred to as profiles. Generally amorphous polymers are used in profile extrusion to avoid the shrinking that takes place during crystallization processes. The asymmetric nature of the products from this process requires special resin properties such as high melt strength at low melt viscosities and shear thinning melt rheology. The amorphous copolymers of the present invention exhibit improved shear thinning behavior.

[0021] Referring to the accompanying Figures, Figure 1 shows melt viscosity shear rate curves at 260°C for several polymers: (1) PETG is a copolyester comprises a diacid component comprising 100 mole percent terephthalic acid residues and a diol component comprising 69 mole percent ethylene glycol residues and 31 mole percent CHDM residues and is commercially available as EASTAR® 6763 Copolyester from Eastman Chemical Company; (2) PROVISTA™ copolyester (also available from Eastman Chemical Company), which is specifically designed to shear thin by adding branching agents, has a composition similar to PETG; and (3) the copolyester of Example 10 of the present invention. Surprisingly, Example 10 exhibits a shear thinning behavior that resembles the PROVISTA™ copolyester and not the PETG. Similarly, Figure 2 shows melt viscosity shear rate curves at 260°C for the copolyester of Example 8 which shear thins like PROVISTA™ copolyester and not PETG copolyester. For the curves constituting Figures 1 and 2, the complex

viscosity was determined by a Rheonmetrics Dynamic Analyzer (RDA II) with 25 mm diameter parallel plates, 1 mm gap and 10% strain at 260°C. The samples were dried at 60°C for 24 hours in a vacuum oven before the frequency sweep test.

[0022] Thus, based on the shear thinning properties described in Figures 1 and 2, another embodiment of the present invention is a profile produced by profile extrusion comprising an amorphous copolyester composition having an inherent viscosity of at least 0.5 dL/g and comprising:

- (1) a diacid component consisting essentially of about 90 to 100 mole percent terephthalic acid residues and 0 to about 10 mole percent isophthalic acid residues; and
- (2) a diol component consisting essentially of about 10 to about 70 mole percent 1,4-cyclohexanedimethanol residues and about 90 to about 30 mole percent neopentyl glycol residues;

wherein the amorphous copolymers comprises 100 mole percent diacid component and 100 mole percent diol component.

[0023] Further, another embodiment is an injection molded article comprising an amorphous copolyester consisting essentially of an acid component of residues of at least 90 mole percent terephthalic acid and a glycol component of residues of about 10 to about 70 mole percent 1,4-cyclohexanedimethanol and about 90 to about 30 mole percent neopentyl glycol, based on 100 mole percent acid component and 100 mole percent glycol component.

[0024] The copolymers of the invention also may be used to manufacture shaped articles by extrusion blow molding processes. Such processes typically comprise the steps of (1) extruding a copolyester through a die to form a tube of molten copolyester; (2) positioning a mold having the desired finished shape around the tube of molten copolyester; and (3) introducing a gas into the tube of molten copolyester, causing the extrudate to stretch and expand to fill the mold.

EXAMPLES

[0025] The following Examples are intended to illustrate, but not limit, the scope of the present invention. The inherent viscosities were measured at a temperature of 25°C at 0.5 g/dL concentration in a solvent mixture of symmetric tetrachloroethane and phenol having a weight ratio of symmetric tetrachloroethane to phenol of 2:3. The 2nd cycle glass transition temperatures were determined according to DSC at a heating rate of 20°C/min to a temperature of 280-300°C, quenching in liquid nitrogen to 0°C, and then rerunning the sample and recording the T_g as the 2nd cycle glass transition temperature. Final copolyester compositions were determined by proton NMR analysis on a 600 MHz JEOL instrument.

EXAMPLE 1

[0026] A copolyester comprising a diacid component consisting of 100 mole percent terephthalic acid residues and a diol component consisting of 66 mole percent CHDM residues and 34 mole percent NPG residues (hereinafter referenced as 100T/85CHDM/15NPG) was prepared. Dimethyl terephthalate (DMT; 77.6 g, 0.4 mole), NPG (28.91 g, 0.28 moles), CHDM (46.37 g, 0.32 moles), and 1.49 ml of a solution containing 15 g of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml single-neck, round-bottom flask. The flask was immersed in a Belmont metal bath that was pre-heated to 200°C. Immediately after the flask was immersed the temperature set point was increased to 220°C, and held for 1 hour. After the hour at 220°C the temperature was increased to 260°C, and held for 30 minutes. After this time the theoretical amount of methanol was collected. The pressure in the flask then was reduced from atmospheric to 0.5 Torr. When the pressure had been reduced to 0.5 Torr the temperature set point was raised to 280°C. Stirring was reduced as the viscosity increased until a stir rate of 15 revolutions per minute (RPM) was obtained. The vacuum was discontinued and nitrogen was bled into the flask. The polymer was allowed to solidify by cooling to a temperature below T_g, removed from the flask and ground to pass through a 3 mm

screen. The inherent viscosity of the polymer was 0.895 dL/g. The polymer had a 2nd cycle T_g of 87.82°C. Compositional analysis (by NMR) showed the diol component of the copolyester consisted of 66.1 mole percent CHDM residues and 33.9 mole percent NPG residues.

EXAMPLE 2

[0027] A copolyester having the composition 100T/61CHDM/39NPG was prepared. DMT (77.60 g, 0.40 moles), NPG 33.70 grams (0.33 moles) of NPG, 39.74 grams (0.28 moles) of CHDM, and 1.49 ml of a solution containing 15 grams of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml single neck round bottom flask and reacted and polymerized according to the procedure described in Example 1. The inherent viscosity of the polymer was 0.930 dL/g. The polymer had a 2nd cycle T_g of 86.70°C with no crystalline melting point observed, and compositional analysis showed that the diol component of the copolyester consisted of 61.4 mole percent CHDM residues and 38.6 mole percent NPG residues.

EXAMPLE 3

[0028] A copolyester having the composition 100T/56CHDM/44NPG was prepared. DMT (77.6 g, 0.40 moles), NPG (38.48 g, 0.37 moles), CHDM (33.12 g, 0.23 moles), and 1.47 ml of a solution containing 15 g of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml, single-neck, round-bottom flask and reacted and polymerized according to the procedure described in Example 1. The inherent viscosity of the polymer was 0.938 dL/g. The polymer had a 2nd cycle T_g of 85.90°C with no crystalline melting point observed, and compositional analysis showed that the diol component of the copolyester consisted of 55.8 mole percent CHDM and 44.2 mole percent NPG residues.

EXAMPLE 4

[0029] A copolyester having the composition 100T/45CHDM/55NPG was prepared. DMT (77.60 g, 0.4 moles), NPG (43.26 g, 0.42 moles), CHDM (26.50 g, 0.18 moles), and 1.44 ml of a solution containing 15 g of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml single neck round bottom flask and reacted and polymerized according to the procedure described in Example 1. The inherent viscosity of the polymer was 0.897 dL/g. The polymer had a 2nd cycle Tg of 83.66°C with no crystalline melting point observed, and compositional analysis showed the diol component of the copolyester consisted of 44.7 mole percent CHDM and 55.3 mole percent NPG residues.

EXAMPLE 5

[0030] A copolyester having the composition 100T/32CHDM/68NPG was prepared. DMT (77.60 g, 0.4 moles), NPG (48.05 g, 0.46 moles), CHDM (19.87 g, 0.14 moles), and 1.42 ml of a solution containing 15 g of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml single neck round bottom flask and reacted and polymerized according to the procedure described in Example 1. The inherent viscosity of the polymer was 1.143 dL/g. The polymer had a 2nd cycle Tg of 82.43°C with no crystalline melting point observed, and compositional analysis showed the diol component of the copolyester consisted of 32.3 mole percent CHDM and 67.7 mole percent NPG residues.

EXAMPLE 6

[0031] A copolyester having the composition 100T/21CHDM/79NPG was prepared. DMT (77.60 g, 0.4 moles), NPG (52.83 g, 0.51 moles), CHDM (13.25 g, 0.09 moles), and 1.40 ml of a solution containing 15 g of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml single neck round bottom flask and reacted and polymerized according to the procedure described in Example 1. The inherent viscosity of the polymer was 0.925 dL/g. The polymer had a 2nd cycle Tg of 80.30°C

with no crystalline melting point observed, and compositional analysis showed the diol component of the copolyester consisted of 21.4 mole percent CHDM and 78.6 mole percent NPG residues.

EXAMPLE 7

[0032] A copolyester having the composition 100T/15CHDM/85NPG was prepared. DMT (77.60 g, 0.4 moles), NPG (57.62 g, 0.55 moles), CHDM (6.62 g, 0.05 moles), and 1.37 ml of a solution containing 15 g of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml single neck round bottom flask and reacted and polymerized according to the procedure described in Example 1. The inherent viscosity of the polymer was 0.863 dL/g. The polymer had a 2nd cycle Tg of 77.78°C with no crystalline melting point observed, and compositional analysis showed the diol component of the copolyester consisted of 14.6 mole percent CHDM and 85.4 mole percent NPG residues.

EXAMPLE 8

[0033] A copolyester having the composition 100T/67CHDM/33NPG was manufactured in a batch pilot plant reactor. DMT (10.215 kg, 22.5 pounds), NPG (4.495 kg, 9.9 pounds), CHDM (5.153 kg, 11.35 pounds), and 53.4 g of a solution of titanium isopropoxide in n-butanol were charged into a 68.13 liter (18-gallon) batch reactor with intermeshing spiral agitators and a distillation column. The agitators were operated forward for 50 minutes and then reversed for 10 minutes. The internal temperature was increased to 200°C and held for 2 hours. The temperature then was increased to 260°C and held for 30 minutes. At this time, the weight of distillate was recorded and the temperature was increased to 280°C. Upon reaching 280°C the weight of distillate again was recorded. The agitator was changed to switch directions every 6 minutes, and vacuum was applied at a rate of 13 Torr/minute until full vacuum (0.5 Torr) was reached. The polymerization mixture was maintained for 25 minutes at 45 rpm, and then maintained for 15 minutes at 10 rpm. The copolyester

thus obtained then was immediately extruded and chopped into pellets. The polymer had an inherent viscosity of 0.791 dL/g, and a 2nd cycle Tg of 87.48°C with no crystalline melting point observed. Compositional analysis (by NMR) showed the diol component of the copolyester consisted of 67.4 mole percent CHDM residues and 32.6 mole percent NPG residues. The color values, using the CIE lab color system, were as follows: L* 82.28, a* -0.44, b* 3.80.

EXAMPLE 9

[0034] A copolyester having the composition 100T/45CHDM/55NPG was produced in a batch pilot plant reactor. DMT (10.669 kg, 23.5 pounds), NPG (6.220 kg, 13.7 pounds), CHDM (3.223 kg, 7.1 pounds), and 53.4 g of a solution of titanium isopropoxide in n-butanol were charged into a 68.13 liter (18-gallon) batch reactor with intermeshing spiral agitators and a distillation column. After charging the raw materials, the manufacturing procedure described in Example 10 was repeated. The resulting polymer had an inherent viscosity of 0.844 dL/g, and a 2nd cycle Tg of 84.08°C with no crystalline melting point observed. Compositional analysis (by NMR) showed the diol component of the copolyester consisted 45.4 mole percent CHDM residues and 54.6 mole percent NPG residues. The color values were as follows: L* 83.19, a* -0.27, b* 3.97.

EXAMPLE 10

[0035] Example 9 was repeated except that the polycondensation was modified to produce a copolyester having a lower IV. After reaching full vacuum (0.5 Torr), the agitator was held at 25 rpm for only 30 minutes, and then held for 15 minutes at 10 rpm. The copolyester polymer then was immediately extruded and chopped into pellets. The copolyester polymer had an inherent viscosity of 0.713 dL/g, and a 2nd cycle Tg of 83.41°C with no crystalline melting point observed. Compositional analysis (by NMR) showed the diol component of the copolyester consisted of 44.1

mole percent CHDM and 55.9 mole percent NPG. The color values were as follows: L* 82.79, a* -0.40, b* 3.15.

[0036] The resistance of the following amorphous copolymers to attack or degradation by lipid solutions was evaluated:

Copolyester I: PETG 6763, a commercially-available amorphous polyester wherein the diacid component consists of 100 mole percent terephthalic acid residues and the diol component consisting of about 69 mole percent EG residues and 31 mole percent CHDM residues; IV=0.71.

Copolyester II: PCTG 5445, a commercially-available amorphous polyester wherein the diacid component consists of 100 mole percent terephthalic acid residues and the diol component consisting of about 38 mole percent EG residues and 62 mole percent CHDM residues; IV=0.72.

Copolyester III: Amorphous copolyester of Example 8.

Copolyester IV: Amorphous copolyester of Example 9.

Standard tensile test bars (ASTM-D638) of each of the copolymers I, II, III, and IV were prepared by injection molding. The bars were placed on three-point-bend strain rigs at fixed strains of 0, 0.5, 1.5 and 2.7% while simultaneously being exposed to Liposyn II 20% intravenous fat emulsion (lipid solution) for 72 hours. Exposure to the lipid solution was accomplished by placing a 2.54 mm X 1.77 mm (1 inch X 0.5 inch) patch of filter paper over the center of the bar and saturating the patch with the lipid solution initially and then rewetting several times a day. The treated bars were then subjected to tensile testing according to ASTM D638. The results of these tensile tests are shown in Table I wherein the values given for the experimental strain conditions (Condition Strain), Yield Strain, and Elongation at Break are percentages. Yield Stress and Break Stress are given in megapascals. Each test bar was inspected before and after the evaluation and given a rating of A=no change, B=slightly crazed, C=moderately crazed, and D=severely crazed. Similar resistance tests were run with IPA instead of lipid, with these results shown in Table II wherein

the values are the same as those for Table I. The control represents samples prior to contact with lipid solution. An inspection of Tables I and II clearly shows that the amorphous copolyester of the present invention exhibit better overall performance than the corresponding commercial amorphous copolyester I and II. The superior performance is manifested, in general, by the maintenance of a satisfactory appearance and the maintenance of high elongation to break after exposure to the lipid while under strain.

TABLE I

<u>Copolyester</u>	<u>Condition</u> <u>Strain</u>	<u>Yield</u> <u>Strain</u>	<u>Elongation</u> <u>to Break</u>	<u>Yield</u> <u>Stress</u>	<u>Break</u> <u>Stress</u>	<u>Appearance</u>
I	Control	5.3	167	48.6	29.2	
I	0	5.3	65.4	51.1	25.5	A
I	0.5	5.3	63.2	50.5	25.1	A
I	1.5	5.3	40	51.5	25.2	D
I	2.7	5.2	51.3	49.8	25.9	B
II	Control	4.7	285	43.4	40.7	
II	0	-	-	-	-	-
II	0.5	4.9	289.5	46.7	43.8	A
II	1.5	4.9	296.0	46.8	43.3	A
II	2.7	-	6.9	-	29.5	D
III	Control	5.7	178.9	43.8	46.8	
III	0	5.3	154.9	45.1	43.1	A
III	0.5	5.3	148.3	45	41.7	A
III	1.5	5.4	137.7	45.6	40.9	C
III	2.7	5.5	140.5	44.9	42.1	B
IV	Control	5.3	134.1	47.4	42.9	
IV	0	5	102.9	48.4	36.4	A
IV	0.5	5.1	99.6	48.8	37.9	A
IV	1.5	5.2	24.7	49	36.6	C
IV	2.7	5.2	18.1	48	36.9	C

TABLE II

<u>Copolyester</u>	<u>Condition</u>	<u>Yield</u>	<u>Elongation</u>	<u>Yield</u>	<u>Break</u>	<u>Appearance</u>
	<u>Strain</u>	<u>Strain</u>	<u>to Break</u>	<u>Stress</u>	<u>Stress</u>	
I	Control	5.3	167	48.6	29.2	
I	0	5.3	79	50.5	25.5	A
I	0.5	5.3	36.7	50.3	25.2	C
I	1.5	5.3	61.7	45.6	25.1	C
I	2.7	7	26.6	41.1	25.9	D
II	Control	4.7	285	43.4	40.7	
II	0	-	-	-	-	-
II	0.5	5	287.7	46.3	43.5	D
II	1.5	5.1	296.0	38.1	40.2	D
II	2.7	7.3	6.9	33.2	39.5	D
III	Control	5.7	178.9	43.8	46.8	
III	0	5.1	161	45.1	44.7	A
III	0.5	5.2	159.4	44.8	43.8	B
III	1.5	5.6	125	44.7	38.9	C
III	2.7	5.7	150	42.1	42.9	D
IV	Control	5.3	134.1	47.4	42.9	
IV	0	5.1	114.9	48.1	38.1	A
IV	0.5	5.1	104.5	48.3	36.9	B
IV	1.5	4.3	4.3	42.5	42.5	C
IV	2.7	5.2	5.2	36.4	36.4	D

EXAMPLE 11

[0037] A copolyester having the composition 100T/64CHDM/36NPG was produced in a batch pilot plant reactor. DMT (10.215 kg, 22.5 pounds), NPG (4.495 kg, 9.9 pounds), CHDM (5.153 kg, 11.35 pounds), and 53.4 grams of a solution of titanium isopropoxide in n-butanol were charged into a 68.13 liter (18-gallon) batch reactor with intermeshing spiral agitators and a distillation column. The agitator was

operated forward for 50 minutes and then reversed for 10 minutes. The internal temperature was increased to 200°C and held for 2 hours. The temperature was then increased to 260°C and maintained for 30 minutes. After this, the weight of distillate was recorded and the temperature was increased to 280°C. Upon reaching 280°C the weight of distillate was again recorded. The agitator was changed to switch directions every 6 minutes, and vacuum was applied at 13 Torr/minute until full vacuum (0.5 Torr) was reached and held for 45 minutes at 25 rpm. The copolyester polymer obtained then was immediately extruded, and chopped into pellets. The polymer had an inherent viscosity of 0.678 dL/g. Compositional analysis (by NMR) showed the diol component of the copolyester consisted of 63.9 mole percent CHDM residues and 36.1 mole percent NPG residues. The color values were as follows: L* 82.58, a* -0.66, b* 4.76.

EXAMPLE 12

[0038] A copolyester having the composition 100T/38CHDM/62NPG was produced in a batch pilot plant reactor. DMT (10.669 kg, 23.5 pounds), NPG (6.220, 13.7 pounds), CHDM (3.223, 7.1 pounds), and 53.4 grams of a solution of titanium isopropoxide in n-butanol were charged into a 68.13 liter (18-gallon) batch reactor with intermeshing spiral agitators and a distillation column. The agitator was operated forward for 50 minutes and then reversed for 10 minutes. The internal temperature was increased to 200°C and maintained for 2 hours. The temperature was then increased to 260°C and maintained for 30 minutes. After this, the weight of distillate was recorded and the temperature was increased to 280°C. Upon reaching 280°C the weight of distillate was again recorded. The agitator was changed to switch directions every 6 minutes, and vacuum was applied at 13 Torr/minute until full vacuum (0.5 Torr) was reached and maintained for 45 minutes at 25 rpm. The copolyester polymer obtained then was immediately extruded and chopped into pellets. The polymer had an inherent viscosity of 0.692 dL/g. Compositional analysis (by NMR) showed the diol component of the copolyester contained 38.1 mole percent

CHDM residues and 61.9 mole percent NPG residues. The color values were as follows: L* 83.04, a* -0.39, b* 4.60.

[0039] The hydrolytic stability of the following amorphous copolyester polymers was compared:

Polymers I and II: Same as Copolymers I and II defined above.

Polymer V: Copolyester of Example 11

Polymer IV: Copolyester of Example 12

The procedure used in determining loss in molecular weight as a result of hydrolysis involved placing a sample of the copolyester into the barrel of a capillary rheometer and then heating to either 250°C or 280°C and holding for the specified time. The sample was removed, after this treatment, and the molecular weight was determined by standard size exclusion chromatography. The molecular weight loss was calculated from the equation 1- M_w/M_o where M_w is the molecular weight after treatment and M_o is the original molecular weight. The higher the number the greater the weight loss. The values listed in the "hydrolysis" rows are undried samples, while those listed in the "thermal" rows refer to samples dried at 60°C for 48 hours at a vacuum of approximately 5 Torr. The results are shown in Table III.

TABLE III

	Melt Temp	Melt Time	Molecular Weight Loss			
			Polymer I	Polymer II	Polymer V	Polymer VI
Hydrolysis	250	5	0.24	0.1	0.05	0.05
Hydrolysis	250	7	0.32	0.15	0.05	0.02
Hydrolysis	250	10	0.43	0.22	0.07	0.01
Hydrolysis	250	15	0.57	0.28	0.11	0.05
Thermal	250	5	0.02	0.02	0.08	0
Thermal	250	7	0.03	0.01	0.08	0.08
Thermal	250	10	0.02	0.02	0.12	0.05
Thermal	250	15	0.02	0.03	0.09	0.07
Hydrolysis	280	5	0.47	0.24	0.07	0
Hydrolysis	280	7	0.61	0.36	0.07	0.02
Hydrolysis	280	10	0.68	0.44	0.07	0.03
Hydrolysis	280	15	0.67	0.57	0.15	0.07
Thermal	280	5	0.07	0.08	0.13	0.1
Thermal	280	7	0.07	0.07	0.16	0.13
Thermal	280	10	0.06	0.06	0.2	0.16
Thermal	280	15	0.1	0.08	0.22	0.19

EXAMPLE 13

[0040] A copolyester having the composition 100T/49CHDM/51NPG was prepared. DMT (97 g, 0.5 moles), NPG (48.9 g, 0.47 moles), CHDM (40.7 g, 0.28 moles), and 1.26 ml of a solution containing 15 g of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml single neck round bottom flask and reacted and polymerized according to the procedure described in Example 1. The inherent viscosity of the polymer was 0.49 dL/g. The polymer had a 2nd cycle Tg of 82.2°C with no crystalline melting point observed, and compositional analysis showed the diol component of the copolyester consisted of 49 mole percent CHDM and 51 mole percent NPG residues.

[0041] The procedure of Example 13 was repeated eight times to obtain sufficient polymer for molding and evaluation. The NMR composition (mole percent), inherent viscosity (dL/g) and 2nd cycle DSC Tg (°C) of each of the polymers obtained from the repetitions are shown below. The copolyesters obtained from Example 13 and the repetitions thereof were combined and mixed prior to molding.

Composition	IV	2 nd cycle DSC Tg
T, 50NPG, 50CHDM	0.52	83.4
T, 50NPG, 50CHDM	0.51	83.2
T, 51NPG, 49CHDM	0.52	83.1
T, 50NPG, 50CHDM	0.50	83.3
T, 50NPG, 50CHDM	0.51	82.8
T, 51NPG, 49CHDM	0.51	82.2
T, 50NPG, 50CHDM	0.52	82.3
T, 50NPG, 50CHDM	0.52	82.5

EXAMPLE 14

[0042] A copolyester having the composition 100T/50CHDM/50NPG was prepared. DMT (97 g, 0.5 moles), NPG (48.9 g, 0.47 moles), CHDM (40.7 g, 0.28 moles), and 1.26 ml of a solution containing 15 g of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml single neck round bottom flask and reacted and polymerized according to the procedure described in Example 1. The inherent viscosity of the polymer was 0.56 dL/g. The polymer had a 2nd cycle Tg of 84°C with no crystalline melting point observed, and compositional analysis showed the diol component of the copolyester consisted of 50 mole percent CHDM and 50 mole percent NPG residues.

[0043] The procedure of Example 14 was repeated six times to obtain sufficient polymer for molding and evaluation. The NMR composition (mole percent), inherent

viscosity (dL/g) and 2nd cycle DSC Tg (°C) of each of the polymers obtained from the repetitions are shown below. The copolyesters obtained from Example 14 and the repetitions thereof were combined and mixed prior to molding.

Composition	IV	2 nd cycle DSC Tg
T, 50NPG, 50CHDM	0.54	83.3
T, 50NPG, 50CHDM	0.55	82.7
T, 50NPG, 50CHDM	0.54	83.9
T, 50NPG, 50CHDM	0.56	83.6
T, 50NPG, 50CHDM	0.56	83.2
T, 49NPG, 51CHDM	0.54	82.8

EXAMPLE 15

[0044] A copolyester having the composition 100T/49CHDM/51NPG was produced in a batch pilot plant reactor. DMT (10.646 kg, 23.5 pounds), NPG (6.214 kg, 13.7 pounds), CHDM (3.234 kg, 7.1 pounds), and 26.7 grams of a solution of titanium isopropoxide in n-butanol were charged into a 68.13 liter (18-gallon) batch reactor with intermeshing spiral agitators and a distillation column. The agitator was operated forward for 50 minutes and then reversed for 10 minutes. The internal temperature was increased to 200°C and held for 2 hours. The temperature was then increased to 260°C and maintained for 30 minutes. After this, the weight of distillate was recorded and the temperature was increased to 280°C. Upon reaching 280°C the weight of distillate was again recorded. The agitator was changed to switch directions every 6 minutes, and vacuum was applied at 13 Torr/minute until full vacuum (0.5 Torr) was reached and held until a 750 wattmeter increase or a peak. The copolyester polymer obtained then was immediately extruded, and chopped into pellets. The polymer had an inherent viscosity of 0.77 dL/g. Compositional analysis (by NMR) showed the diol

component of the copolyester consisted of 49.3 mole percent CHDM residues and 50.7 mole percent NPG residues.

COMPARATIVE EXAMPLE 1

[0045] A copolyester having the composition 100T/48CHDM/52NPG was prepared. DMT (97.0 g, 0.5 moles), NPG (48.9 g, 0.47 moles), CHDM (40.7 g, 0.28 moles), and 0.63 ml of a solution containing 15 g of titanium tetraisopropoxide in 250 ml of n-butanol were added to a 500 ml single neck round bottom flask. The flask was immersed in a Belmont metal bath that was preheated to 200°C. Immediately after the flask was immersed the temperature was increased to and held at 220°C for 2.5 hours. The temperature then was increased to and held at 260°C for 30 minutes. After this time the theoretical methanol was collected. The pressure in the flask was then reduced from atmospheric to 0.5 Torr. When the pressure had been reduced to 0.5 Torr(6 minutes), the temperature set point was then raised to 280°C. Approximately 5 minutes after raising the temperature set point to 280°C, stirring was reduced from 200 rpm to 100 rpm and held for 10 minutes. The vaccum was discontinued and nitrogen was bled into the flask. The polymer was allowed to solidify by cooling to a temperature below T_g, removed from the flask and then ground to pass through a 3 mm screen. The inherent viscosity of the polymer was 0.29 dL/g. The polymer had a 2nd cycle DSC T_g of 75.4°C and compositional analysis by NMR showed the diol component of the copolyester consisted of 48 mole percent CHDM and 52 mole percent NPG residues.

[0046] The procedure of Comparative Example 1 was repeated eight times to obtain sufficient polymer for molding and evaluation. The NMR composition (mole percent), inherent viscosity (dL/g) and 2nd cycle DSC T_g (°C) of each of the polymers obtained from the repetitions of Comparative Example 1 are shown below. The copolymers obtained from Comparative Example 1 and the repetitions thereof were combined and mixed prior to molding.

Composition	IV	2 nd cycle DSC Tg
T, 52NPG, 48CHDM	0.31	77.1
T, 52NPG, 48CHDM	0.31	75.6
T, 52NPG, 48CHDM	0.37	79.1
T, 52NPG, 48CHDM	0.36	78.4
T, 52NPG, 48CHDM	0.29	74.0
T, 52NPG, 48CHDM	0.34	78.5
T, 52NPG, 48CHDM	0.34	78.2
T, 52NPG, 48CHDM	0.33	78.1

[0047] Standard tensile test bars (ASTM-D638) were prepared by injection molding each of the copolymers Examples 13, 14, 15 and Comparative Example 1 and subjected to tensile testing according to ASTM D638, flexural testing according to ASTM D790 and Unnotched Izod Impact Strength at 23°C according to ASTM D256. The results of these tests are shown in Table IV wherein the values given for Yield Strain and Break Strain are percentages, Yield Stress, Break Stress and Modulus are given in pounds per square inch. The inherent viscosities (IV, dL/g) were measured prior to molding.

TABLE IV

Example	13	14	15	C-1
IV	0.51	0.56	0.77	0.33
Flexural				
Yield Strain	5.01	5.1	4.8	1.96
Yield Stress	9380	9313	9495	4888
Modulus	269738	265031	278381	252056
Tensile				
Yield Strain	5.36	5.24	5.2	2.4
Yield Stress	6493	6526	6461	3534
Break Stress	4921	7518	8695	3534
Break Strain Elongation to break	92.98	180	180.16	2.4
Izod				
Unnotched	80% No Break	80% No Break	100% No Break	100% Break
	>16 ft-lb/inch	>16 ft-lb/inch	>16 ft-lb/inch	0.51 ft-lb/inch

The low molecular weight copolyester of Comparative Example 1 (IV=0.33), similar to the copolyester exemplified in U.S. Patent 4,551,403, exhibits an elongation to break of only 2.4% whereas the elongation to break of the Example 13 copolyester (IV=0.51) is 92.98%. These elongation to break values go to 180% for copolymers having IV's of 0.56 and 0.77. The elongation to break values demonstrate the excellent and useful mechanical properties for the copolymers having IV's of greater than 0.5 dL/g. In addition, the unnotched Izod impact value for the copolyester of Comparative Example 1 was only 0.51 foot-pounds per inch with 100% of the test bars breaking during the test. This unnotched Izod impact value indicate that the Comparative Example 1 copolyester is a very brittle material and is contrasted to the 80% no break for the copolymers of Examples 13 and 14 and 100% no break for the

copolyester of Example 15. The higher molecular weight copolymers of Examples 13, 14 and 15 therefore are non-brittle, tough useful materials. The copolyester of Comparative Example 1 was so brittle that it was almost impossible to mold test bars for the mechanical property evaluation. Thus, the low molecular weight copolyester of Comparative Example 1 is of no value as a molding or extrusion copolyester. In contrast, the copolymers having IV's greater than 0.5 dL/g have excellent mechanical properties.

EXAMPLE 16

[0048] A copolyester comprising a diacid component consisting of 100 mole percent terephthalic acid residues and a diol component consisting of 60 mole percent CHDM residues and 40 mole percent NPG residues (hereinafter referenced as 100T/60CHDM/40NPG) was melt-phase polymerized in a 65 gallon (245 liter) stainless steel batch reactor with intermeshing spiral agitators. To the reactor was added 39.64 kg (87.39 pounds, 204.5 moles) of dimethyl terephthalate, 11.48 kg (25.30 pounds, 110.4 moles) of neopentyl glycol (NPG), 28.25 kg (62.27 pounds, 196.3 moles) of 1,4-cyclohexanedimethanol (CHDM) and 112.56 grams of a butanol solution containing the titanium catalyst. The reactor was heated to 200°C and held for 2 hours with agitation at 25 RPM. The temperature was increased to 260°C and held for 30 minutes. The temperature was increased to 270°C and the pressure was reduced at a rate of 13 torr per minute to full vacuum. After the vacuum reached <4000 microns (<4 torr), these conditions were held for 1 hour and 15 minutes at 25 RPM. The RPM was reduced to 15 RPM and the conditions held to a wattmeter peak. The pressure was increased to atmospheric with nitrogen and the copolymer was pelletized.

[0049] Bottles were prepared using an 80 mm Bekum H-121 continuous extrusion blow molding machine fitted with a barrier screw. The copolymer had a melt phase inherent viscosity (IV) of 0.719, color values of L* = 55.20, a* = 0.28, b* = 17.76, and a composition by Nuclear Magnetic Resonance (NMR) of 100T/60CHDM40NPG. The

materials were dried for 8 hours at 65°C (150°F) prior to extrusion. The extruder was run at 21 revolutions per minute (RPM) using a 200°C (392°F) barrel temperature and a 190°C (375°F) head temperature. The temperature of the melt was 218°C (425°F), measured by inserting a melt probe directly into the parison 5mm out from the die. The materials were extruded into water bottles having a volume of 3.785 liters (1 U.S. gallon), using a 100 mm die. The bottles weighed between 140 and 190 grams.

EXAMPLE 17

[0050] A copolyester comprising a diacid component consisting of 100 mole percent terephthalic acid residues and a diol component consisting of 56 mole percent CHDM residues and 44 mole percent NPG residues (hereinafter referenced as 100T/56CHDM/44NPG) was melt-phase polymerized in a 65 gallon (245 liter) stainless steel batch reactor with intermeshing spiral agitators. To the reactor was added 39.64 kg (87.39 pounds, 204.5 moles) of dimethyl terephthalate, 11.48 kg (25.30 pounds, 110.4 moles) of neopentyl glycol (NPG), 28.25 kg (62.27 pounds, 196.3 moles) of 1,4-cyclohexanedimethanol (CHDM) and 112.56 grams of a butanol solution containing the titanium catalyst. The reactor was heated to 200°C and held for 2 hours with agitation at 25 RPM. The temperature was increased to 260°C and held for 30 minutes. The temperature was increased to 270°C and the pressure was reduced at a rate of 13 torr per minute to full vacuum. After the vacuum reached <4000 microns (<4 torr), these conditions were held for 1 hour and 15 minutes at 25 RPM. The RPM was reduced to 15 RPM and the conditions held to a wattmeter peak. The pressure was increased to atmospheric with nitrogen and the copolymer was pelletized.

[0051] Bottles were prepared using an 80 mm Bekum H-121 continuous extrusion blow molding machine fitted with a barrier screw containing a Maddock mixing section. The copolymer had a melt phase inherent viscosity (IV) of 0.725, color values of L* = 50.50, a* = -2.46, b* = 2.50, and a composition by Nuclear Magnetic

Resonance (NMR) of 100T/56CHDM44NPG. The materials were dried for 8 hours at 65°C (150°F) prior to extrusion. The extruder was run at 10 revolutions per minute (RPM) using a 190°C (375°F) barrel temperature and a 185°C (365°F) head temperature. The temperature of the melt was 212°C (413°F), measured by inserting a melt probe directly into the parison 5 mm out from the die. The materials were extruded into handleware juice bottles having a volume of 1.89 liters (64 ounces), using a 70 mm die. The bottles weighed between 70 and 80 grams.

[0052] The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.